

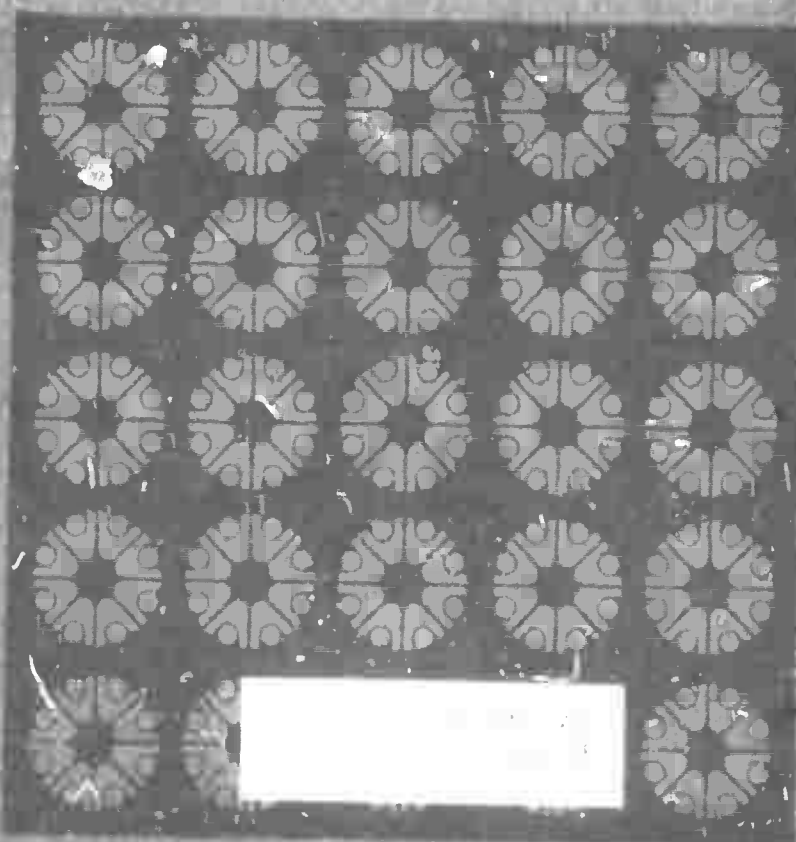
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Semi Annual Technical Report for the Period
2 Nov. 1971 to 1 May 1972

INVESTIGATION OF THE INFLUENCE OF STRUCTURE ON
CHEMICAL STABILITY AND THERMAL/MECHANICAL
SHOCK PROPERTIES OF GLASS-LIKE CARBONS

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SUMMARY

Glass-like carbons have potential for meeting the demands for high temperature applications in defense, space, and civilian applications. In spite of this potential, relatively little research has been conducted to exploit the promising properties of these materials. This study was instituted one year ago, along with three other ARPA-sponsored contracts, to investigate the properties of a variety of glass-like carbons (or more descriptively unstructured carbons) and to develop techniques for fabrication of these materials.

This program was designed specifically to investigate the chemical reactivity and the thermal and mechanical shock resistance of glass-like carbons. During the past reporting period, we have extended the reactivity studies to include a porous glass-like carbon material and a pyrolytic carbon called low temperature isotropic (LTI) pyrolyte. The pyrolyte is similar in appearance and many of its properties are similar to the more conventional glass-like carbons, but has a substantially higher reactivity to flowing oxygen in the temperature range from 300-600°C.

The porous glass-like carbon material has a surface area of about 50 m²/g and, thus, bulk samples exhibit a somewhat higher reactivity than pure glass-like carbons with a surface area less than 0.1 m²/g. However, if the reactivity is expressed in rate per unit surface area, the porous materials are lower than crystalline graphite by a factor 10 to 100.

Shock resistance has been expressed in a quantitative fashion by determining the work of fracture during mechanical shock and the thermal stress gradients generated during thermal shock. These tests have shown that small pores in the material produce a more controlled fracture though no decrease in the work of fracture was observed. On the other hand, fiber reinforcement in the material produced a profound increase in the work of fracture indicating a substantial increase in toughness.

The thermal shock tests have shown a sizable increase in the thermal stress resistance of glass-like carbons with an increase in heat-treatment temperature from 1000 C to 2900°C. However, the calculated stress levels at fracture are lower by a factor of ten than expected from strength values. The low fracture stress was attributed to surface imperfections in the samples producing stress risers leading to premature fracture.

Thermal diffusivity and heat capacity measurements were required for the calculation of thermal stress gradients. These measurements have also proven to be a useful aid in obtaining structural information. A substantial increase in thermal diffusivity was observed with increasing heat-treatment temperature. This measurement appears to be a sensitive measure of the degree of structural order, the higher thermal diffusivity corresponding to a more ordered structure.

Preliminary specific heat measurements have been made on glass-like carbon samples over a narrow temperature range between 77 and 107°C. Small but consistent decreases in specific heat were observed with an increase in heat treatment temperature. This observation also correlates well with previous observations for graphite where specific heat decreases occur as the degree of crystallinity increases.

Future work on this program will cover a wider range of temperatures and are expected to increase our understanding of the relationship of glass-like carbon properties to structural features.

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Dr. Garth L. Tingey

INTRODUCTION

The need for improved high-temperature materials for our advancing technology is stimulating increased interest in glass-like carbons. These materials have been reported⁽¹⁾ to have higher strength and lower reactivity than other forms of carbon, yet they maintain the advantage of excellent high temperature properties.

Since the publication of the first series of semi-annual reports⁽²⁻⁵⁾ on the ARPA-sponsored programs, we have noted a sizable increase in interest in glass-like carbons from various governmental and private organizations as evidenced by the number of requests for information.

During the period covered by this report, we have continued the work previously reported⁽²⁾ on reactivity and on the shock properties of a variety of glass-like carbons. This work has been expanded to include a wider variety of materials; specifically, the reactivity of a porous glass-like carbon produced at the University of Michigan⁽³⁾ and a pyrolytic carbon material produced at Gulf Energy and Environmental Systems Company⁽⁵⁾ have now been measured. In the traditional sense of the term, these materials may not be considered to be glass-like. The porous materials were made from a solid polymer by pyrolysis, as are the commercial materials, but they are processed in larger dimensions and heat treated under conditions selected to develop a material containing varying amounts of porosity.⁽³⁾ The pyrolytic samples were fabricated in a fluidized

bed by pyrolysis of propane.⁽⁵⁾ They are amorphous in structure and have an appearance quite similar to glass-like carbons. The pyrolytes are produced with a variety of properties (i.e., density, strength, etc.) determined by the pyrolysis conditions.

In addition to studies of reactivity and shock properties, we have studied the thermal diffusivity and heat capacity of some of the glass-like carbon samples. This work was undertaken to supply the fundamental data required for the analysis of the shock properties in terms of structural parameters. These studies are also expected to add to the general understanding of structure of glass-like carbons.

This report describes our results obtained during this reporting period in the following areas:

- Chemical Reactivity and Surface Area.
- Work of Fracture Testing.
- Thermal Shock Testing.
- Thermal Conductivity.
- Heat Capacity.

1. Chemical Stability of Glass-Like Carbons

The rate at which glass-like carbons react with a variety of chemical species has been reported⁽¹⁾ to be significantly lower than that of other forms of carbon. Earlier results⁽²⁾ from our laboratory have shown that the reactivity of glass-like carbons to flowing oxygen is highly variable. For example, the reactivity of a single glass-like carbon sample processed at 1000°C has been shown to decrease by three orders of magnitude when heat treated to 2900°C. Presumably, the major effect of the heat treatment is to purify the sample, thus, decreasing the effect of catalytic impurities.

We have previously suggested that the low reactivity for glass-like carbons is a direct result of low permeability and, thus, a low surface area for reaction to occur. Therefore, during the period covered by this report, we have determined the reactivity of porous glass-like carbons produced by Prof. Hucke's group⁽³⁾ at the University of Michigan. These materials have a surface area high enough to be readily measured. Thus, the change in surface area with heat treatment and oxidation has been determined on these higher surface area samples.

The following is a description of the experimental approach and the results of the reactivity measurements.

Experimental Approach

Results have been previously reported⁽²⁾ on the reactivity measurements of four types of carbons as follows:

- (1) TSX - nuclear-grade graphite.
- (2) Tokai Electrode Manufacturing Company, Ltd., "Glassy Carbon."
- (3) Le Carbone Lorraine produced "Carbone Vitreux."
- (4) "LTI Pyrolyte" produced by the Gulf Energy and Environmental Systems Company.

This report contains additional information on the LTI Pyrolyte and also includes data on a porous glass-like carbon material produced at the University of Michigan.

The experimental details for the measurement of the reactivity of the samples to flowing oxygen was described in the earlier progress report.⁽²⁾

Heat Treatment

Samples have been heat treated to determine the effect of heat treatment temperature on the reactivity of glass-like carbon. For this investigation, several samples of various types of glass-like carbon were heated inductively using a graphite susceptor in an argon atmosphere and maintained at temperature for one hour. During this process, the samples lost a small amount of mass (normally 1-2%) but were unchanged in their general appearance, except for a slight color change from black to gray.

Surface Area Determination

The surface area was determined for some samples with an area great enough to measure ($> 0.2 \text{ m}^2/\text{gm}$). This determination was made by measuring the low-temperature (95°K) absorptivity of nitrogen on the carbon surface and calculating the surface area by the BET equations. In some cases involving low permeability materials, the samples were powdered to generate sufficient area to study. The samples were powdered using a high-purity aluminum oxide mortar and pestle and then screened through a standard 230-mesh screen. The reactivity of the powdered material was then measured by the technique described⁽²⁾ and compared with that of bulk samples.

Results and Conclusions

The rates of reaction of a variety of types of glass-like carbon to flowing oxygen are shown in Table I. For completeness, this table includes the data reported earlier,⁽²⁾ as well as that obtained during this reporting period.

As previously observed, there is a marked dependence of reactivity upon heat treatment temperature. In all cases, heat treatment to 2900°C substantially reduced the reactivity of the material. The "glassy" carbon samples manufactured by Tokai were measured as received for all heat treatments, but all other glass-like carbon types were heat treated to

TABLE I. Reactivity of Glass-Like Carbons.

| Carbon Type | Heat Treatment Temperature °C | Density g/ml | Ash Content ppm | Rate Constant g/g-hr | Rate at 800°K g/g-hr | Surface Area m ² /g |
|--------------------------|-------------------------------|--------------|-----------------|-------------------------------------|-----------------------|--------------------------------|
| TSX - Nuclear Graphite | 3000 | 1.71 | 10-100 | $3.4 \times 10^9 e^{-42,700/RT}$ | 7.3×10^{-3} | 0.7 |
| Tokai - Glassy Carbon | | | | | | |
| GC-10 | 1000 | 1.49 | 1000-2000 | $6.2 \times 10^6 e^{-32,000/RT}$ | 11.0×10^{-3} | |
| GC-20 | 2000 | 1.48 | 1000-2000 | $3.2 \times 10^4 e^{-23,600/RT}$ | 11.0×10^{-3} | |
| GC-30 (0-6% oxidized) | 3000 | 1.45 | 70-1000 | $5.4 \times 10^3 e^{-24,000/RT}$ | 1.5×10^{-3} | |
| GC-30 (17% oxidized) | 3000 | -- | -- | $2.5 \times 10^5 e^{-33,500/RT}$ | 0.18×10^{-3} | |
| Carbon Vitreux | | | | | | |
| V-1 | 1000 | 1.5 | 200 | $1.9 \times 10^7 e^{-28,600/RT}$ | 290×10^{-3} | |
| V-2 | 2000 | | | $3.5 \times 10^6 e^{-35,000/RT}$ | 1.0×10^{-3} | |
| V-3 | 2900 | | | $7.6 \times 10^6 e^{-38,800/RT}$ | 0.2×10^{-3} | |
| V-3 (powdered) | 2900 | | | $9.3 \times 10^7 e^{-32,700/RT}$ | 108×10^{-3} | 5.8 |
| LTI Pyrolyte | | | | | | |
| 5408-7 | 1350 | 1.97 | | $9.4 \times 10^7 e^{-34,000/RT}$ | 48×10^{-3} | |
| 5408-7 | 2900 | -- | | $7.1 \times 10^{10} e^{-47,200/RT}$ | 9.0×10^{-3} | |
| 5408-17 | 1350 | 1.46 | | $3.2 \times 10^9 e^{-35,900/RT}$ | 500×10^{-3} | |
| 5408-17 | 2900 | -- | | $4.7 \times 10^6 e^{-34,900/RT}$ | 1.4×10^{-3} | |
| 5408-17 (17% oxidized) | 2900 | -- | | $7.2 \times 10^7 e^{-35,300/RT}$ | 16×10^{-3} | |
| 5408-35 | 1475 | 1.46 | | $1.7 \times 10^9 e^{-37,800/RT}$ | 80×10^{-3} | |
| Porous Glass-Like Carbon | | | | | | |
| 312-30 | 2000 | -- | | $3.5 \times 10^8 e^{-33,800/RT}$ | 204×10^3 | 44 |
| 312-30 | 2900 | -- | | $2.7 \times 10^8 e^{-39,000/RT}$ | 6×10^{-3} | 52 |
| 312-30 (13% oxidized) | 2900 | -- | | $5.6 \times 10^9 e^{-39,000/RT}$ | 124×10^{-3} | 390 |
| 312-30 (powdered) | 2900 | -- | | $1.1 \times 10^6 e^{-26,300/RT}$ | 72×10^{-3} | 83 |

2900°C in our laboratory by the procedure described in the previous section. We have previously shown⁽²⁾ by microscopic observations that impurities are removed from the glass-like carbons during heat treatment. It is, thus, assumed that at least part of the reduction in reactivity is due to removal of catalytic impurities. If this were the major cause of the reduced reactivity, one would expect an increase in the apparent activation energy of the rate constant. Although there is generally a trend to increasing activation energy for the higher heat-treated samples, it is not always so and the increases which are found are not significantly greater than the sample-to-sample variations observed. In spite of the attempts to maintain high purity during the powdering and screening operation, a lower activation energy for the reaction with powdered samples is observed, thus, indicating an increase in the concentration of catalytic impurities.

The reactivity data appear to confirm the earlier suggestions that glass-like carbons exhibit an inherent reactivity lower than other carbon forms. This difference, however, is quite small for the reaction with gaseous oxygen and can be readily masked by small differences in the concentration of catalytic impurities, by surface area differences, or by other properties which tend to cause an increase in the reactivity of the sample. The reactivity to oxygen at this temperature is, however, not a very sensitive test because of its inherent high rate of reaction and relatively low selectivity. In fact, it is reasonable to expect that more selective chemical species which react at significant rates with most carbon types may be quite unreactive to glass-like carbons.

It is of substantial interest then to determine the structural or chemical characteristics which cause this lower reactivity. We have already suggested that the lower reactivity of glass-like carbons may be entirely due to the low surface area. In fact, it would seem that strictly from an energy basis that the unstructured or glass-like materials may tend to be more reactive than a crystalline material like graphite. Microscopic studies of oxidation of graphite have shown⁽⁶⁾ that edge-plane atoms of carbon react at a rate 10^{13} times more rapidly than basal-plane

atoms. If one assumes a truly amorphous state for glass-like carbon, an assumption which is certainly not entirely correct, he would describe all atoms as edge-type atoms. On this basis, therefore, one might expect glass-like carbon to have a much higher reactivity than crystalline graphite.

To gain understanding and insight into this question, we have determined the reactivity of glass-like carbons as a function of surface area and normalized the data to unit surface area. It is recognized that a more rigorous determination can be made using the active surface area rather than the total surface area. However, past work with bulk graphite samples has shown that reactivity is quite well correlated with BET area; thus, the BET area appears to be proportional to the active area for such samples. This is apparently not true with all carbons but is expected to hold reasonably well for this work.

Table II shows the effect of surface area on the reactivity of several carbon materials to oxygen as a function of surface area. As seen from the data, the "carbon vitreux" has a reactivity comparable to the graphite sample, but the porous glass-like carbons, especially those heat treated to 2900°C, are from 10 to 100 times less reactive than the graphite. This observation is significant since it confirms the earlier suggestions that glass-like carbons have an inherent reactivity approximately equal to or somewhat less than a rather pure grade of crystalline graphite. One obvious exception to this finding is the pyrolyte carbon, which has a relatively high reactivity even in the bulk form. At present, we have not tested any powdered pyrolyte carbons.

It may be significant that the powdered samples are somewhat more reactive per unit surface area than the bulk samples in the porous glass-like carbons. This, of course, is further confirmation that impurities were added during the powdering and screening process. Perhaps the impurity could be removed by a further heat treatment of the powder at

TABLE II. Surface Area of Glass-Like Carbon.

| Carbon Type | Heat Treatment Temperature °C | Carbon Removed by Oxidation % | Surface Area m ² /g | Reactivity to Flowing O ₂ at 800°K, g/m ² -hr |
|--------------------------|----------------------------------|----------------------------------|-----------------------------------|--|
| TSX - Nuclear Graphite | 3000 | 0 | 0.7 | 1.04×10^{-3} |
| Carbon Vitreux | | | | |
| V-3 (powdered) | 2900 | 0 | 5.8 | 18.6×10^{-3} |
| Porous Glass-Like Carbon | | | | |
| 312-30 | 2000 | 0 | 44.0 | 4.6×10^{-3} |
| 312-30 | 2900 | 0 | 52.0 | 0.1×10^{-3} |
| 312-30 | 2900 | 13 | 390.0 | 0.3×10^{-3} |
| 312-30 (powdered) | 2900 | 0 | 83.0 | 0.9×10^{-3} |

2900°C and yield a material more comparable to the bulk samples, but this experiment has not been conducted.

Another perturbation upon the reaction rate, particularly upon the porous samples, is the effect of in-pore diffusion which could reduce the reactivity, especially at high temperatures. At present, we have seen no indication in the Arrhenius plots that in-pore diffusion is making a significant contribution. Therefore, we assume that diffusion does not have a major effect in these results.

In conclusion, the results of our reactivity studies indicate that the reactivity of glass-like carbons to flowing oxygen is perhaps somewhat less than graphite even when normalized for surface area effects.

It is of possible significance to future uses of porous glass-like carbons to note the large increase in surface area with oxidation. Table II shows that a surface area of nearly 400 m²/g was generated in one sample after removal of only 13% of the carbon by oxidation. The resulting material may be useful as a adsorbate for purification systems or molecular sieves.

II. Work of Fracture Testing

Glass-like carbon, as presently produced, is an extremely brittle, notch-sensitive material. The purpose of this testing was to determine the work of fracture for vitreous carbons as produced today as baseline data. Subsequent testing on other structural variations, such as pores or fibrous reinforcement, provides data which can be compared to the original ones to note areas of greatest potential improvement.

Experimental and Results

In work-of-fracture (WOF) testing, the amount of work necessary to propagate a crack across unit cross section of a sample is determined. The sample is notched in such a way that propagation is stable. The method used is more completely described in Reference (2), as are the initial results which were obtained on "carbone vitreux," both as-received and after heat-treatments. The values are included below for comparison.

TABLE III. Work of Fracture Results.

| <u>Heat Treatment Temperature, °C</u> | <u>Work of Fracture ergs/cm²</u> |
|---|---|
| 1000 | 3.41×10^4 |
| 2000 | 3.77×10^4 |
| 2900 | 2.42×10^4 |

Note: a typographical error in Ref. 2 had WOF units as ergs/cm³.

The maximum for the 2000°C heat-treated material correlates with similar maxima in flexural and impact strength. Strength probably affects these results to cause the maximum. Acoustic emission monitoring showed absolutely no microcracking prior to catastrophic failure.

Porosity may have a beneficial effect in glass-like carbons. Small pores can act as crack blunters and, thus, may make the material more resistant to incidental damage. Samples of porous glass-like carbon, produced

at the University of Michigan, with a density of 0.81 g/cm^3 with pores of about 50 microns in diameter were studied. The work-of-fracture curve and acoustic emission response are plotted in Figure 1. For photomicrographs of the material, see Reference (2).

The average work of fracture of the porous glass-like carbon was $3.8 \times 10^4 \text{ ergs/cm}^2$, about the same as observed for the "carbon vitreux." The acoustic emission curve shows that cracking occurred 15 seconds prior to failure.

A second materials variable important to work of fracture is a reinforcement phase. A material similar to glass-like carbon but containing a reinforcement phase is Carb-i-tex 100, manufactured by Carborundum Corp. This material is a two-dimensional laminate of carbon fibers bonded with carbon binder. Notched bars of Carb-i-tex 100 were cut and tested in their toughest orientation as shown by the inset in the drawing, Figure 2. Figure 2 also shows the work of fracture and acoustic emission curves for a typical specimens. Note the vastly different shape of the WOF curve. The average WOF for the material was $3.18 \times 10^6 \text{ ergs/cm}^2$, two orders of magnitude greater than that obtained with "carbon vitreux." Note also that the acoustic record shows activity virtually from the moment of load application. This indicates that fibers are being broken and/or pulled from the matrix. This process continues as fracture proceeds. Pulling these fibers from the matrix requires a great deal of work, which is the main reason for the large increase in WOF.

The scanning electron micrograph in Figure 3 shows the results of this behavior graphically. The pulled-out-fibers are ten to a hundred times as long as their diameters, indicating that the reinforcement occurring is not the maximum obtainable; the strength and modulus of such a composite probably falls substantially below values indicated by the "Rule of Mixtures." On the other hand, this material is a tough composite. Fiber-matrix interactions determine whether a composite will be strong or

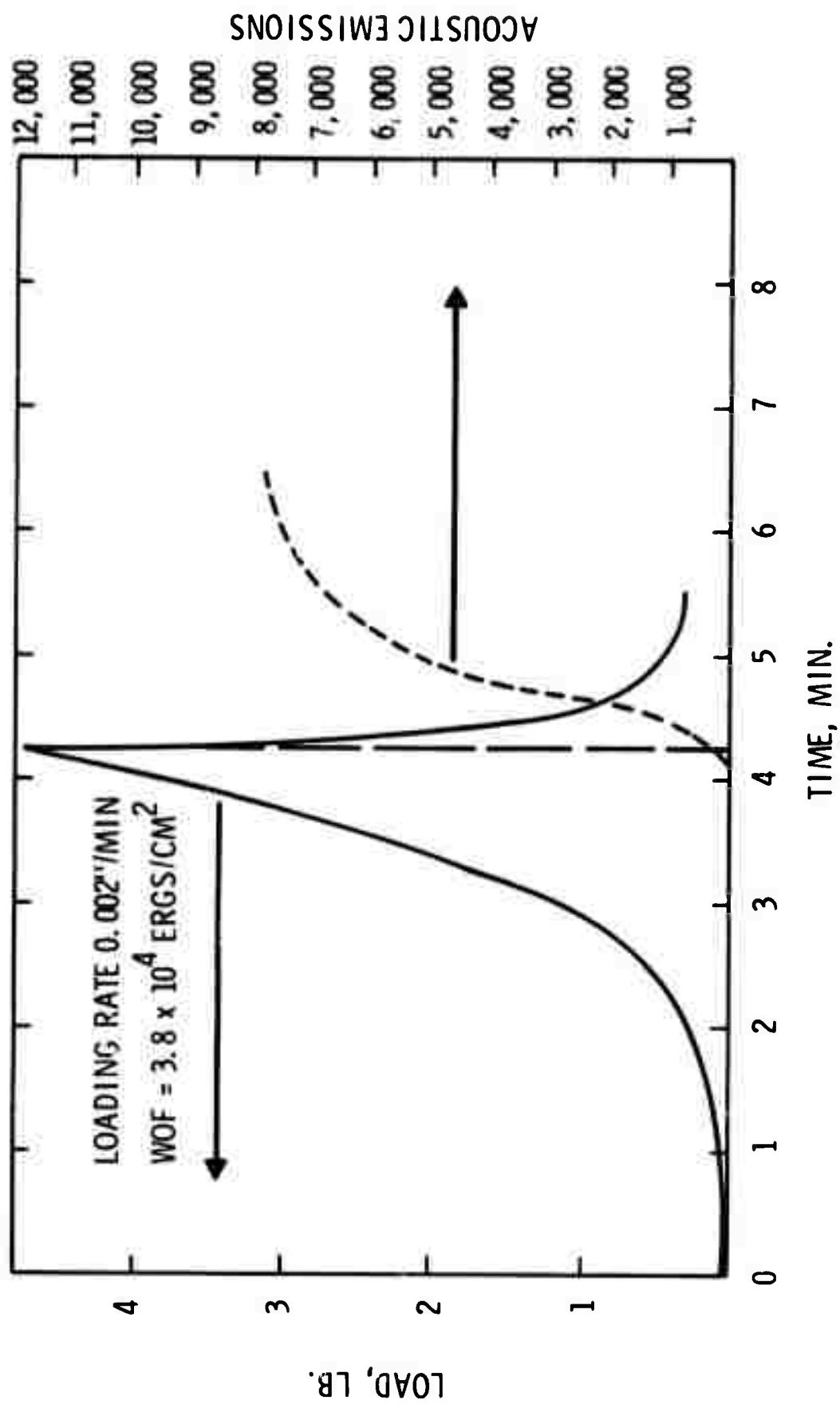


FIGURE 1. Work of Fracture and Acoustic Emission Response for Porous Carbon Sample No. 318.
Machine Speed 0.002 in./min.

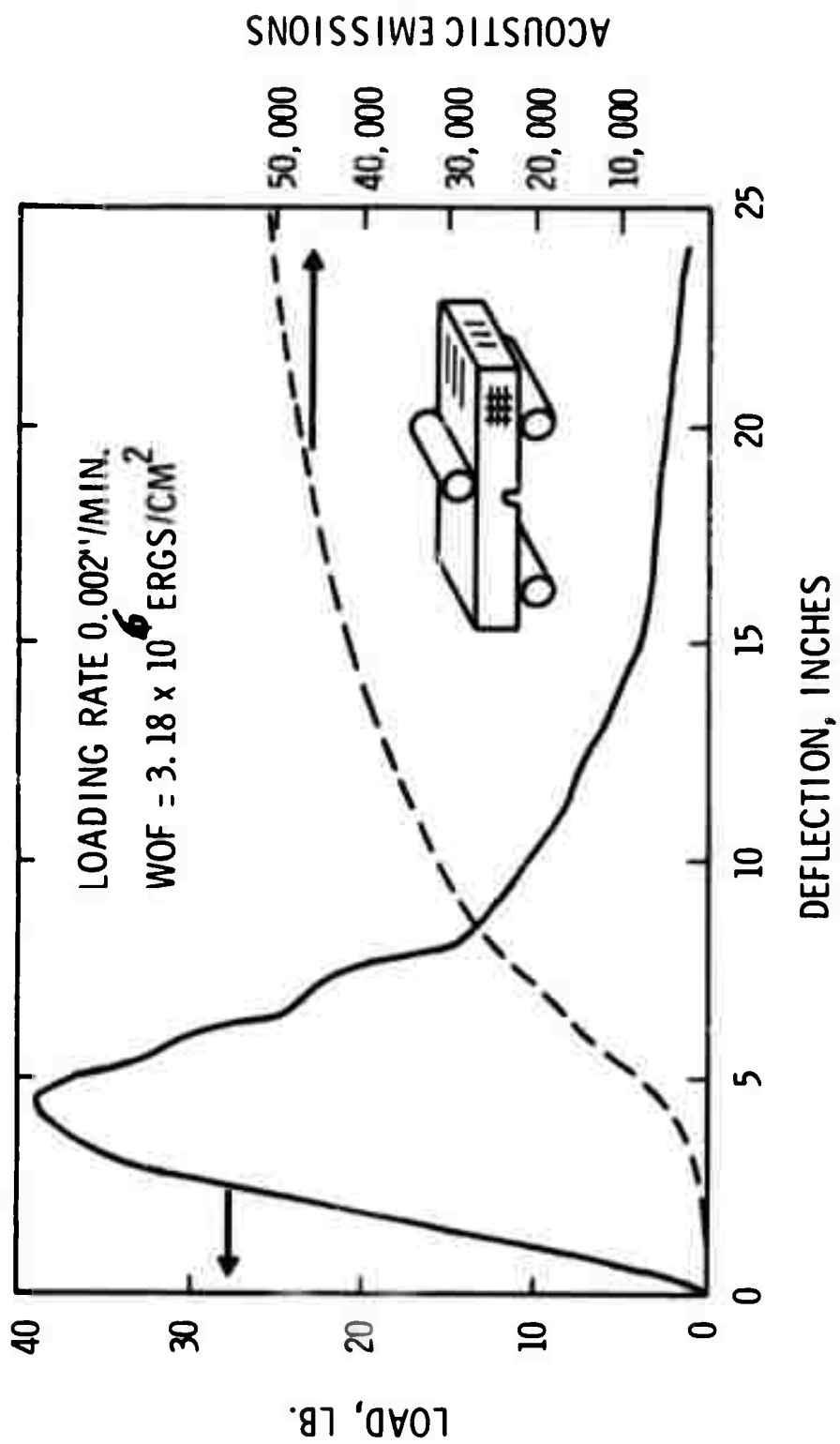


FIGURE 2. Work-of-Fracture Curve and Acoustic Emission Response for Carb-i-tex.
 100 sample. Machine speed 0.002 in./min.



(a)



(b)

FIGURE 3. (a) 100X and (b) 500X Scanning Electron Micrographs Showing Extensive Fiber Pullout in Canex-tex 100. Sample fractured slowly in WOF test.

tough. If fiber-matrix interactions are strong, the elastic modulus and strength will be high, but the material may fail catastrophically. The intended application determines the degree of interaction which yields both required strength and toughness.

Conclusions

The results of our studies on work of fracture lead to the following conclusions:

1. The effect of porosity in glass-carbons is to produce more controlled fracture with no decrease in WOF. The controlled fracture produced acoustic emissions detectable substantially before specimen failure.
2. Introduction of fibers in the carbon-carbon composite tested produced a profound increase in the work of fracture.

III. Thermal Shock Testing

While it is known⁽¹⁾ that vitreous carbon is not as resistant to thermal shock as graphites, the thermal shock resistance has not been quantified in any way. It is our objective to (1) test commercially-available vitreous carbons and (2) analyze the results to suggest means of improving this important property.

Experimental and Results

The thermal shock testing apparatus was described in Reference (2), as were some of the initial values for power required to fracture disc samples. The best data to date, in terms of watts to fracture half the samples tested, are listed in Table IV. These results are for the "carbone vitreux."

TABLE IV. Threshold Power for Thermal Shock of 1 inch Diameter Discs

| Sample | Threshold Power |
|---|-----------------|
| As-received "Carbone Vitreux," 1000°C processed. | 135 watts |
| "Carbone Vitreux," processed 1 hour at 2900°C. | 200 watts |

It is seen that the vitreous carbon is substantially more resistant to thermal shock after heating to 2900°C, in agreement with the data in Reference (1), and in agreement with a simple KS/ E analysis. In order to quantify the stresses involved, the thermal stresses were analyzed in light of two equations from Timoshenko⁽⁷⁾:

$$\sigma_r = \alpha E \left(\frac{1}{b^2} \int_0^b T r dr - \frac{1}{r^2} \int_0^r T r dr \right)$$

$$\sigma_\theta = \alpha E \left(-T + \frac{1}{b^2} \int_0^b T r dr + \frac{1}{r^2} \int_0^r T r dr \right)$$

where

- α = thermal expansion coefficient, in./in.°C.
- E = Young's modulus, psi.
- b = outer radius of disc, inches.
- r = radius, inches.
- T = temperature at the point of interest, at time, t .
- σ_θ = tangential stress, psi.
- σ_r = radial stress, psi.

The most important quantity in the above equations is temperature as a function of radius during heating of discs. This was determined experimentally by monitoring the temperature with a fast-responding infrared pyrometer* as a function of time, at a given point and power level. The area monitored was 1/16 x 1/16 inch. Performing this

* Thermo-Dot, Infrared Industries, Santa Barbara, California.

monitoring as a function of radius enables us to plot temperature as a function of radius and time, as shown in Figure 4. The following cases were selected for further study:

- (1) 1000°C heat-treated "Carbone Vitreux" at a power of 135 watts (its threshold power).
- (2) 2900°C heat-treated material at the same power.
- (3) 2900°C heat-treated material at its threshold power of 200 watts.

These three cases at 12 and 18 seconds after arc initiation were then plotted as the product Tr versus r , see Figure 4 for 12-second data. Graphical integration followed, and σ_r (radial stress) and σ_θ (tangential stress) were calculated. The results are plotted in Figures 5, 6, and 7. In these figures, three factors are apparent:

- (1) The stresses follow the expected trends, with σ_r compressive at a maximum at the sample center. σ_θ is also compressive at the sample center and is maximum tensile at the edge. It is these tensile stresses which cause the sample to crack.
- (2) The calculated stresses are too low, by about 10X compared with strength values in Reference (1). As can be seen by comparing the three figures, the results suggest that 1000 psi is fracture stress for the discs.
- (3) The two samples above threshold power (Case 1 and 3) have higher tensile stresses at their edges than the one tested at a subcritical power (Case 2).

The result (2) above was unexpected, but can be explained by considering the fact that the critical crack stress-intensity factor, K_{IC} , is 44 psi-in.^{1/2} for this material, as determined by our earlier fracture toughness testing. If $K = \sigma\sqrt{\pi a}$, where σ = observed breaking stress, and a is crack width; and if σ is 1000 psi, we can solve for a . The solution shows that a ten-fold strength reduction requires a crack of only about 0.006 in. wide, at the edge of the sample. During this study, we

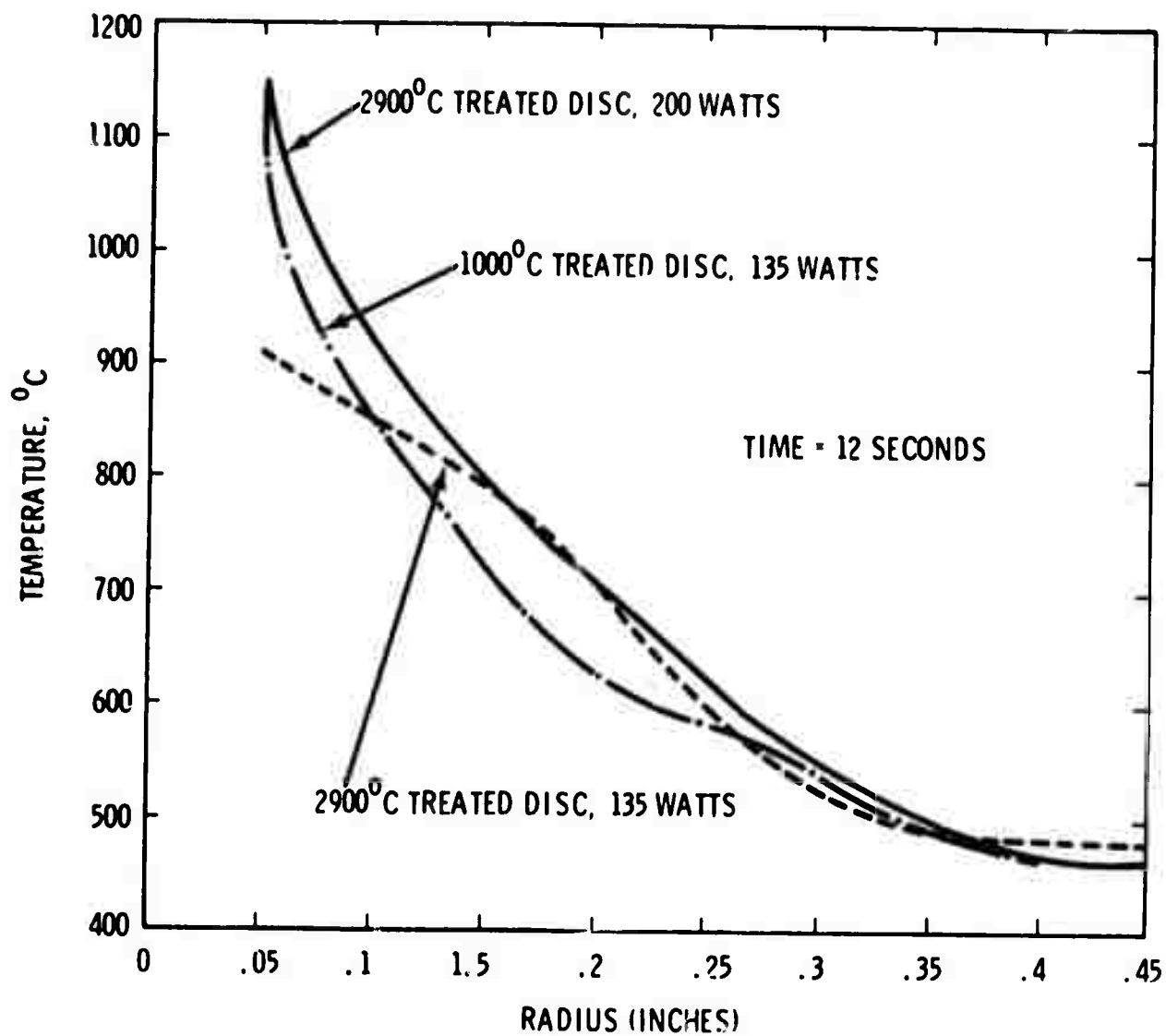


FIGURE 4. Temperature as a Function of Radius at 12 Sec. after Arc Initiation, for the Disc Treatments and Power Levels Shown.

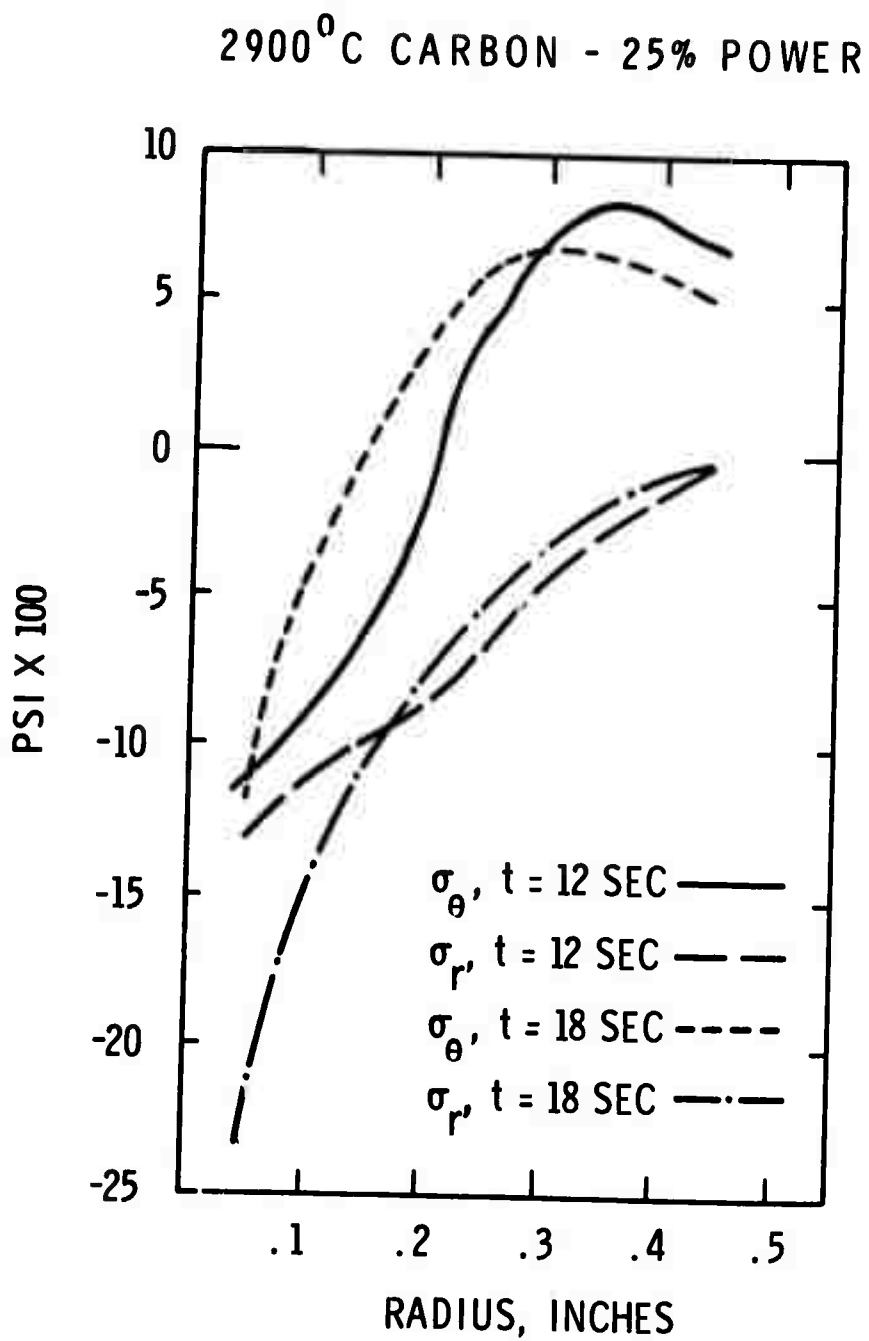


FIGURE 5. Principal Stresses as a Function of Radius, in 2900°C Heat-Treated Disc at 135 Watts Power.

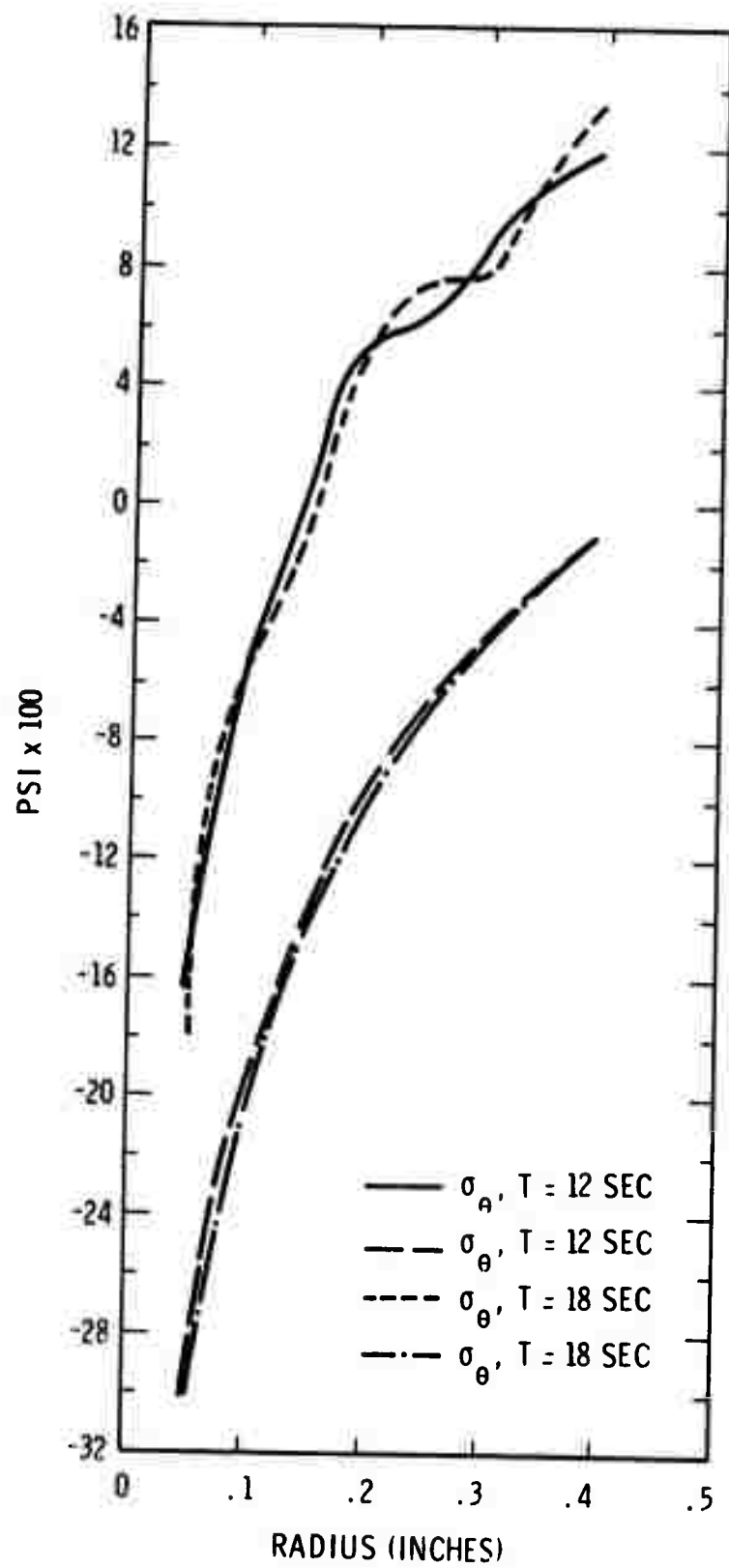


FIGURE 6. Principal Stresses as a Function of Radius, in 1000°C Heat-Treated Disc at 135 Watts Power.

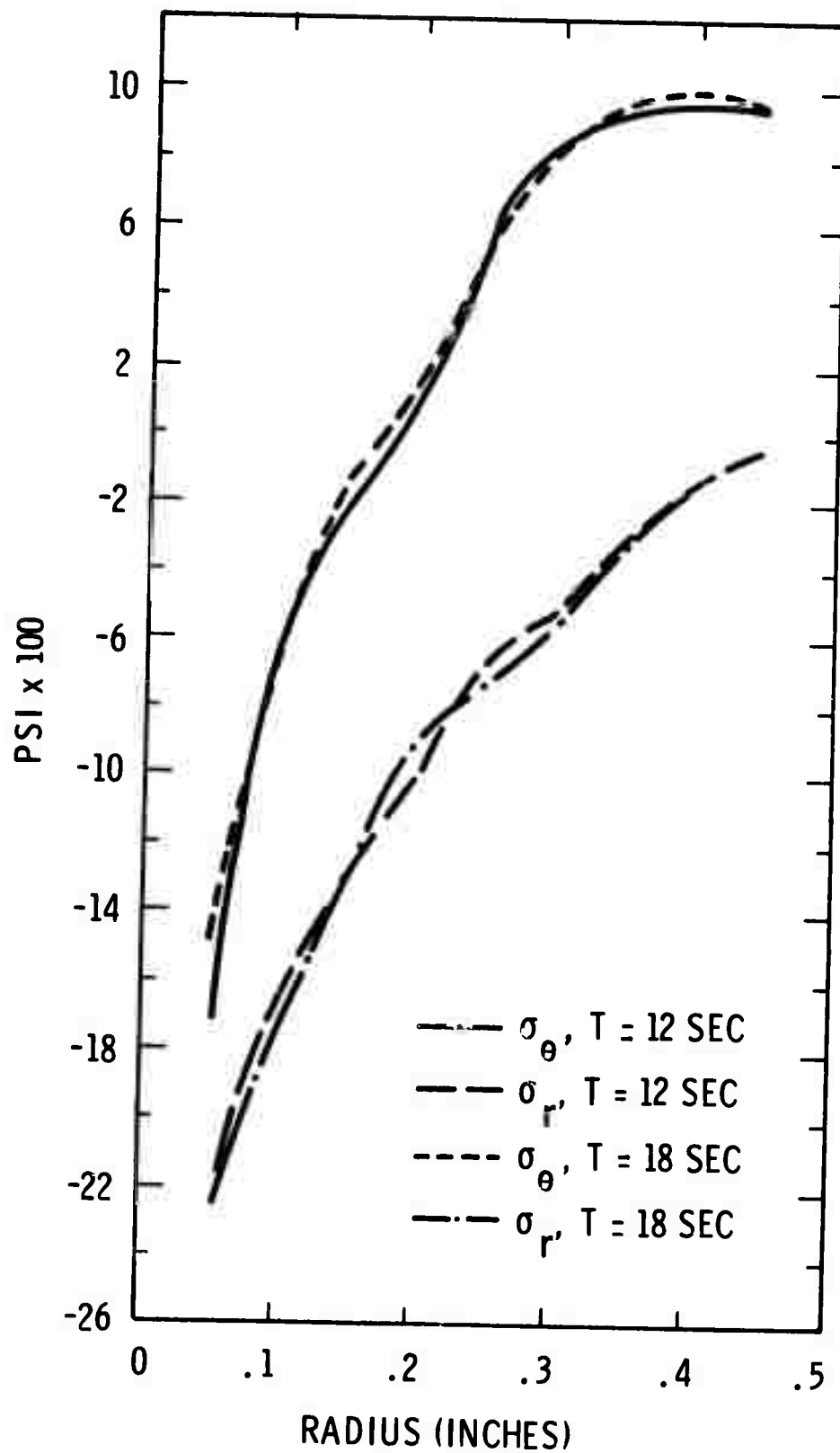


FIGURE 7. Principal Stresses as a Function of Radius, in 2900°C Heat-Treated Disc at 200 Watts Power.

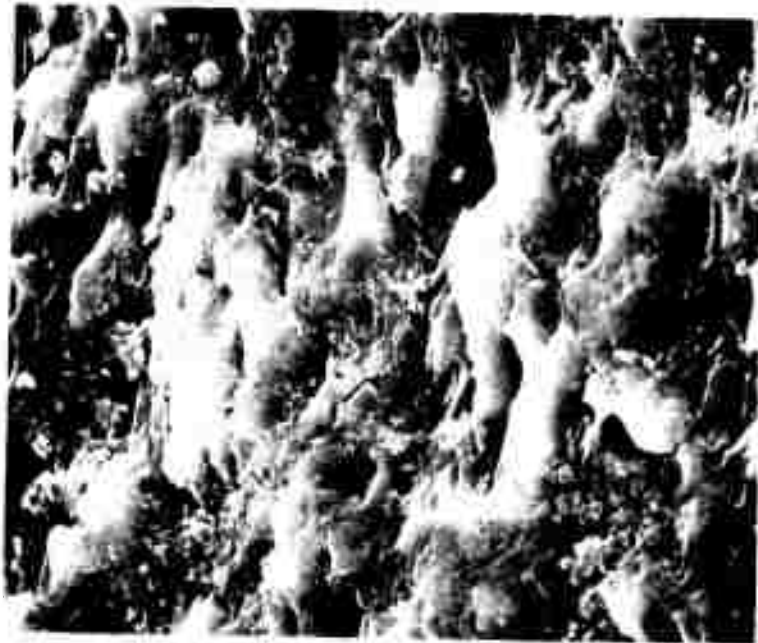
have had difficulty shaping the disc sample for the thermal shock testing. Among the methods used were ultrasonic impact machining, electric discharge machining, and machining with a miniature abrasive grit blaster*; the last being the most satisfactory. One would assume that the surface left by this tool would be rather smooth. In reality, however, the scanning electron microscope shows (Figure 8) that the surface is far from smooth and contains numerous small cracks. These cracks are of themselves too small to explain the strength reduction, but the interaction of these with one of the many pores present could create an effective stress riser. The above is a hypothesis which will be tested shortly by thermal shocking discs with well-polished edges. However, the surface finish on the discs already tested probably represents that likely to result from most forming operations performed on this material. Surface finish, at least in unoxidized samples, is probably very important in its effect on strength.

Conclusions

The main conclusions drawn from these tests are:

1. That the thermal stress resistance of 2900°C heat treated glass-like carbon is substantially greater than that processed at 1000°C.
2. That stresses calculated from Timoshenko's equations follow expected trends but are too low generally to explain specimen failure. Stress risers from cracks at sample edges are a possible explanation.

* *Conco Micro-Blaster, Minarik Electric, Los Angeles, CA.*



(a)



(b)

FIGURE 8. (a) 1000X and (b) 3000X Scanning Electron Micrograph Showing Cracks left by Miniature Grit Blaster in Carbone Vitreux.

IV. Thermal Diffusivity and Specific Heat

The purpose of this work is to provide thermal diffusivity, specific heat, and thermal conductivity data which are required for the quantitative analysis of thermal shock properties of glass-like carbons. In addition, changes will occur in thermal properties which can assist in defining the structure of the various materials investigated.

Relatively few measurements have been made of the thermal properties of glass-like carbon. Yokoyama et al.⁽⁸⁾ have measured from near room temperature to 700°C the thermal diffusivity and heat capacity of a glassy carbon, heat treated to 3000°C. Takahasi and Westrum⁽⁹⁾ have determined the specific heat of a glass-like carbon from 5-350°K. Above 50°K, both investigators found the heat capacity to be essentially the same as that for graphite.

The thermal diffusivity and calculated thermal conductivity⁽⁸⁾ of the 3000°C heat-treated glassy carbon is substantially less than that for a highly crystalline graphite but close to that for graphite with a low degree of graphitization, such as pyrolyte carbon.

Experimental Procedures

Thermal Diffusivity

The thermal diffusivity was measured using a "flash" or "pulse" technique. This method was chosen because of the geometrical restraints of commercially-available glass-like carbons, i.e., plates approximately 0.3 cm thick. The pulse technique, using a radiation source such as a xenon flash tube or laser beam, has been described extensively elsewhere.⁽¹⁰⁻¹²⁾ Briefly, this technique consists of heating one surface of a small specimen disc with a short heat pulse from a laser and subsequently monitoring the thermal response on the opposite surface of the specimen.

Thermal diffusivity (α) can be calculated from the relationship

$$\alpha = \frac{t_0 d^2}{t_{1/2}}$$

where $t_{1/2}$ is the time for the temperature transient on the back surface to reach one half its maximum value, d is the sample thickness, and t_0 is a dimensionless parameter which is a function of the heat losses from the sample and is determined from an analysis of the time - temperature curve.

The thermal diffusivity is related to the thermal conductivity (λ) and heat capacity (C_p) by the relationship

$$\lambda = \alpha \cdot C_p \cdot \rho$$

where ρ is the sample density. This technique, therefore, affords a rapid and convenient method for determining thermal conductivity and thermal diffusivity if the density and heat capacity are known. The technique is also convenient for measuring the diffusivity of the plate-like samples of glass-like carbon used in this study.

The thermal diffusivity was measured in purified argon at one atmosphere pressure in a resistance furnace heated with a tungsten-mesh heater surrounded by tungsten heat shields. A ruby (0.4963 μ) laser provided the heat pulse to the sample. An indium antimonide detector was used to monitor the temperature transients on the back surface of the sample. The output of the detector was displayed on an oscilloscope and recorded on film.

The accuracy of the system has been determined⁽¹²⁾ to 1000°C by measuring the diffusivity of Armco iron and Pyroceram 9606, two suggested standard materials. The results are accurate to $\pm 5\%$ with the published data for iron.⁽¹²⁾ The reproducibility is better than $\pm 3\%$.

The samples of glass-like carbon used in this study were circular discs approximately 0.2 cm thick and 0.635 cm in diameter. They were supported in the furnace on an Al_2O_3 holder. Temperatures were measured with a W - 5% Re versus W - 26% Re thermocouple positioned in the sample holder.

Heat Capacity

The heat capacity was measured with a differential scanning calorimeter. In this apparatus, the sample is subjected to a linear temperature program with the heat flow into the sample being continuously measured. Under these conditions, the heat flow is proportional to the instantaneous specific heat of the sample. Two sample holders are mounted symmetrically inside an enclosure normally held at room temperature. The temperature control system controls the average temperature of the two sample holders with platinum resistance thermometers and heat elements embedded in the sample holders. A secondary temperature control system measures the difference between the two sample holders and adjusts this difference to zero by controlling a differential component of the total heating power. This differential power is measured. Knowing the constants of the system, the temperature rate change, and the power, the specific heat can be calculated. One can also eliminate these parameters if a material of known specific heat is used to calibrate the instrument e.g., $\alpha\text{-Al}_2\text{O}_3$, where the specific heat is known to five significant figures between 0° and 1200°K.

In this study, $\alpha\text{-Al}_2\text{O}_3$ single crystals of two different weights were placed in the reference holder to check the accuracy of the result. Preliminary data indicate an error of less than $\pm 2\%$.

The techniques used for measuring thermal diffusivity and specific heat have an additional advantage in that the same sample can be used for both measurements. In this work, heat capacities were measured following the thermal diffusivity measurements.

Sample Preparation

"Carbon Vitreux" samples, heat treated to 1000°C, were cut from larger plates. Each surface was then lightly ground on 800-mesh abrasive paper to ensure parallel surfaces and to remove possible surface contaminants. Some of the samples were then heat treated for one hour at 2000°C or 2900°C by the technique described in Section 1 of this report. The density of these samples was 1.46 g/cm³.

Porous carbon samples from the University of Michigan (317-39A) were cut from a 2.1 cm diameter right cylinder. The sample density was 0.89 g/cm³ and had been previously heat treated to 2000°C.

Results and Discussion

The thermal diffusivities of the glass-like carbon samples are shown in Figure 9 as a function of temperature up to 1400°C. The data show a substantial increase in diffusivity with increases in heat-treatment temperature. The as-received "Carbon Vitreux" (CV) sample experienced a permanent increase in diffusivity above the heat-treatment temperature (1000°C), as illustrated by the difference between the heating and cooling curves.

An anomalous inflection in the diffusivity curve was observed near 400°C on all samples except for the 2900°C heat treated sample. This effect was observed both on heating and cooling, suggesting a structural effect which is removed only at heat treatment temperatures above 2000°C.

Because the porous sample (317-s9A) was significantly less dense than "Carbon Vitreux," it is difficult to compare diffusivity values.

The thermal diffusivity values of "Carbon Vitreux" (2900°C) are higher than the values reported by Yokoyama, et al.⁽⁸⁾ for a 3000°C heat-treated glass-carbon sample (GC-30) with a density of 1.47 g/cm³.

* CV denotes samples of "Carbon Vitreux" and the number in parentheses denotes the maximum heat-treatment temperature, e.g., CV (1000).

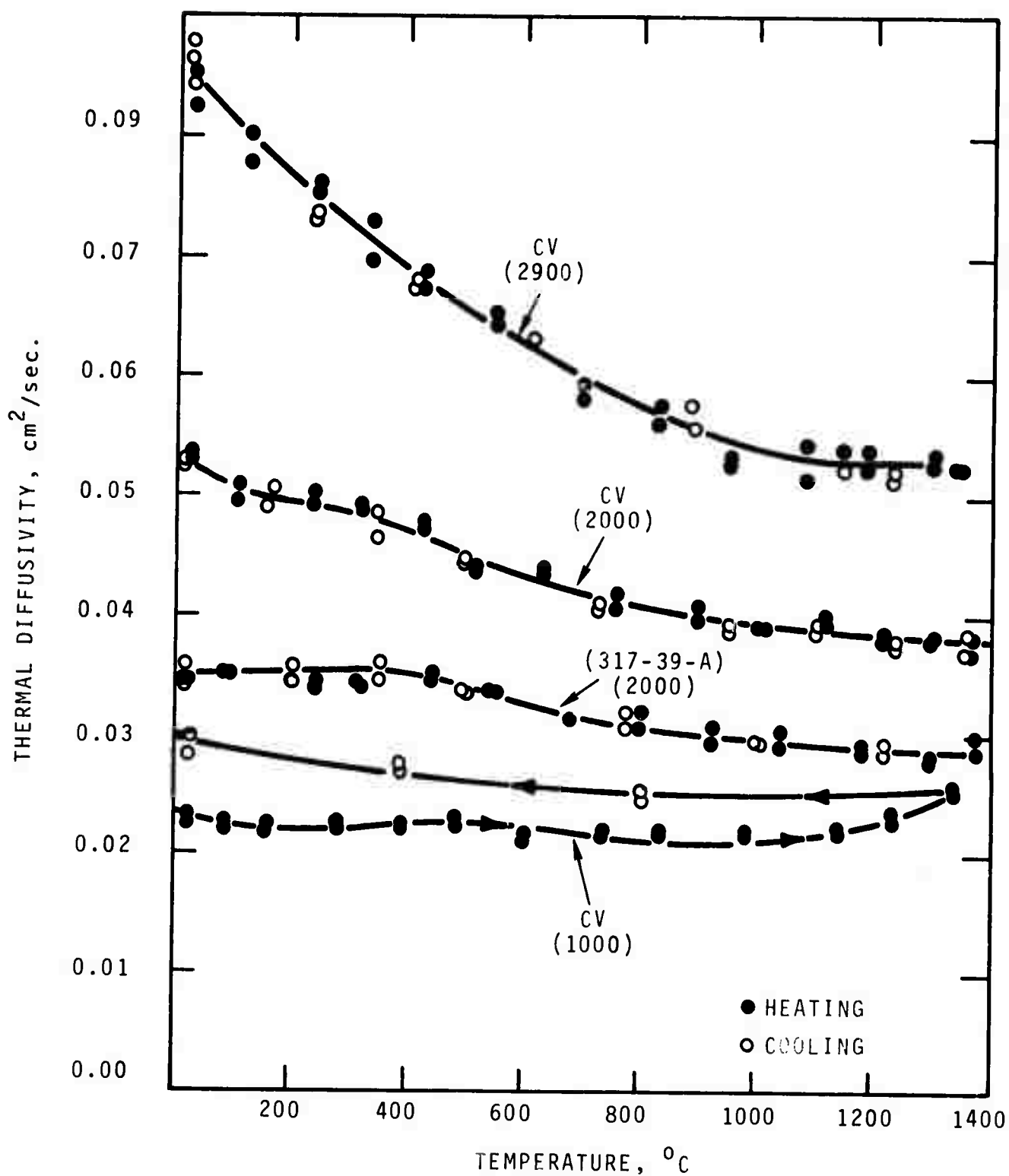


FIGURE 9. Thermal Diffusivity of Vitreous Carbon. CV represents "Carbon Vitreux" and number in parentheses denotes highest heat treatment temperature. Sample 317-39A is a porous carbon from University of Michigan.

The values for GC-30 range from approximately $0.055 \text{ cm}^2/\text{sec}$ at $\sim 40^\circ\text{C}$ to $\sim 0.043 \text{ cm}^2/\text{sec}$ at 700°C which more closely approach our values for the 2000°C heat-treated "carbon vitreux."

The thermal diffusivity obtained for the glass-like carbons are of the same order of magnitude as those reported for some pyrolyte carbons.⁽⁵⁾ Values near room temperature vary from 0.060 to $0.055 \text{ cm}^2/\text{sec}$ for pyrolyte carbons deposited between 1130 and 1355°C with densities 5-35% higher than for the other glass-like carbon, in this study.

The thermal conductivity (λ) was calculated using the measured room temperature density (no correction was made for the volumetric thermal expansion) and the specific heat for ATJ graphite.⁽¹³⁾ These results are summarized in Figure 10 and are compared with reported values for other glass-like carbon⁽⁸⁾ [GC-30 - 3000°C (HTT)] and pyrolyte carbon⁽⁵⁾ of similar density.

The temperature dependence of λ is strikingly different from that for α , increasing rapidly to approximately 400°C with a much smaller dependence at high temperatures. This increase at the lower temperatures appears to result from the rapidly increasing specific heat in this temperature range. The thermal conductivity values for the glassy carbon GC-30 (3000°C) reported by Yokoyama et al.⁽⁸⁾ closely overlaps that of 2000°C heat-treated "Carbon Vitreux." The porous glass-like carbon (317-39A) has a lower thermal conductivity because of the significantly lower density.

Pyrolyte carbon⁽⁵⁾ of comparable density (1.53 g/cm^3) and a moderate deposition temperature (1355°C) has a room temperature thermal diffusivity approximately the same as that of the 1000°C heat-treated "Carbon Vitreux" and the porous glass-like carbon 317-39A (2000°C) but has a significantly different temperature dependence, decreasing with temperature, while the glass-like carbon samples of this study increase with temperature.

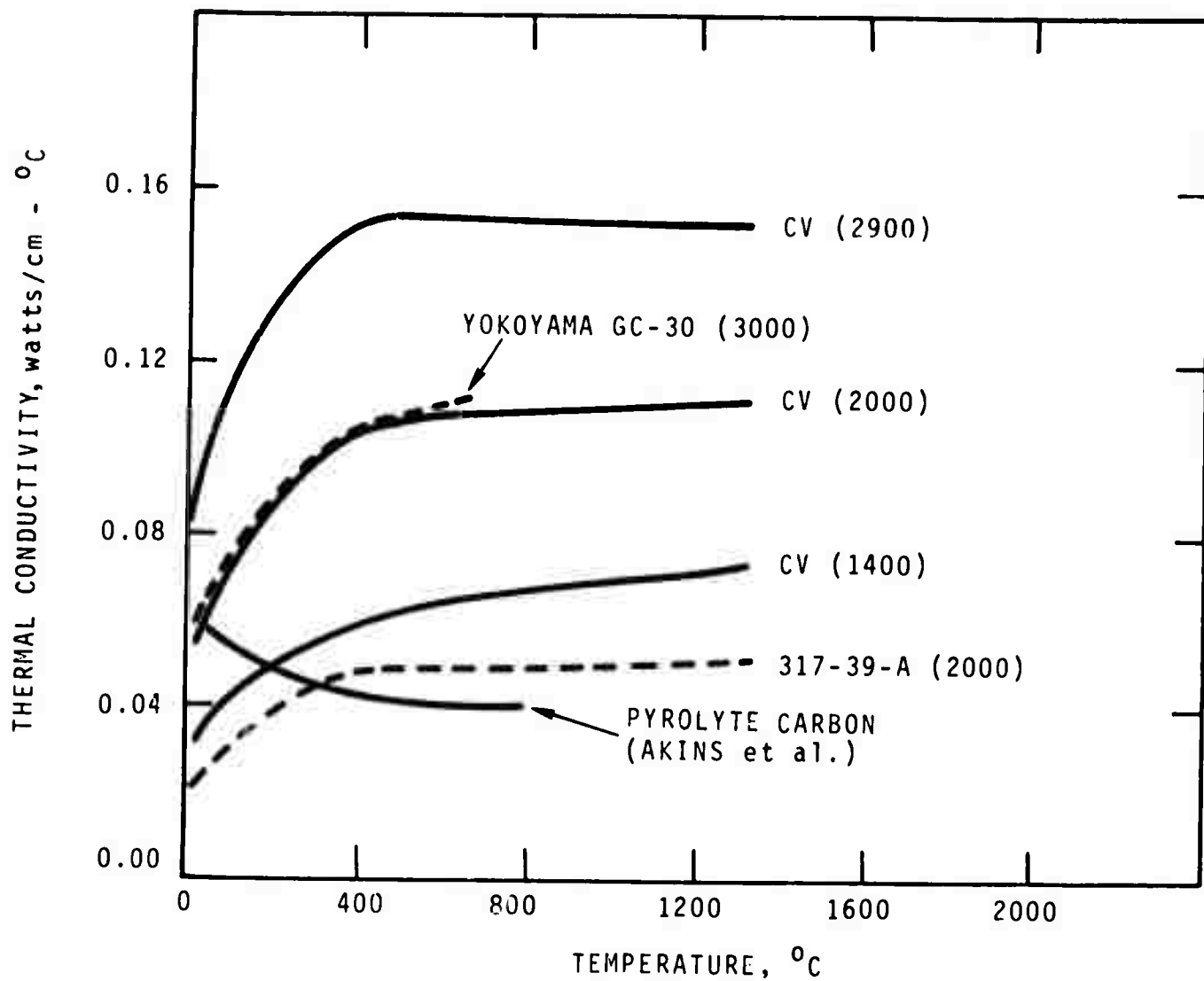


FIGURE 10. Thermal Conductivity of Vitreous Carbon Compared to Other Glass-Like and Pyrolyte Carbons.

These differences in thermal diffusivity resulting from heat treatment and fabrication methods suggest that the thermal diffusivity might be a sensitive measure of the structure of carbon. Those samples with highest ordered structure also appear to have the highest thermal diffusivity values when other factors such as density are held constant.

Specific Heat

Preliminary specific heat measurements were made in a narrow temperature range from 77 to 107°C using the sample on which thermal diffusivity had been previously measured. These preliminary results are tabulated in Table V. The results suggest that the specific heat for the "Carbon Vitreux"(CV) samples decrease with increasing heat treatment temperature, approaching the reported values for graphite. The heat capacity of the CV sample heat treated at 2900°C agrees within 3% of that for GC-30 also treated at 3000°C which has a value very near to that for graphite.

TABLE V. Specific Heat of Glass-Like Carbons.

| <u>Sample</u> | <u>Heat Capacity cal/g-°K</u> | | | |
|--------------------------|-------------------------------|--------------|--------------|--------------|
| | <u>350°K</u> | <u>360°K</u> | <u>370°K</u> | <u>380°K</u> |
| CV (1000°C) | 0.2235 | 0.2325 | 0.2430 | 0.2550 |
| CV (2000°C) | 0.2112 | 0.2196 | 0.2275 | 0.2373 |
| CV (2900°C) | 0.2088 | 0.2168 | 0.2237 | 0.2328 |
| 317-39A (2000°C) | 0.2133 | 0.2254 | 0.2318 | 0.2420 |
| Graphite ⁽¹⁴⁾ | 0.2080 | 0.2138 | 0.2194 | 0.2250 |

These decreases in specific heat resulting from an increased heat-treatment temperature, although small, are consistent and, thus, suggest that the differences are not a result of experimental error. These results are also consistent with reported variations in the low temperature specific heat of graphite⁽¹⁴⁾ which show a decrease in specific heat with an increase in degree of graphitization. One would

deduce that the heat treatment results in an increase in the ordered structure or the crystalline nature of the glass-like carbon. An increase in crystallite size and a higher degree of crystalline perfection is known to lower the specific heat of carbon.⁽¹⁴⁾ Since boron doping does not alter the specific heat while increasing the electrical conduction, one can conclude that the specific heat in poorly graphitized materials results from structural changes and not from impurity or electronic defects. Analogous reasoning could apply to the glass-like carbons.

Thus, the thermal diffusivity/conductivity and, to a lesser degree, the specific heat measurements appear to provide a sensitive tool for studying the structure of glass-like carbons. These properties are possibly sensitive to crystalline perfection, crystallite size, and order. Further studies will be conducted to verify these results and to expand the understanding of these effects.

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